Beyond the solvated electron: the fate of excess charges in molecular liquids

Ilya A. Shkrob and Myran C. Sauer, Jr.

Ionization of dielectric molecular liquids yields positive and negative charges that stabilize in 1-10 picoseconds. What is the nature of these stabilized charges? In some liquids, such as water, saturated alkanes, and ammonia, the excess negative charge exists as a "solvated electron" trapped in a spherical cavity formed by several solvent molecules; the electron density is excluded by these molecules. In other liquids, the excess negative charge "sticks" to the solvent molecule, forming a radical anion. The same happens for the excess positive charge: at any given time, this charge resides on a single molecule, forming a radical cation.

In a series of studies from this laboratory, we have demonstrated that these two scenarios do not exhaust all possibilities. In many liquids, the excess positive or negative charge neither resides in the solvent cavity nor "sticks" to one or two solvent molecules. Instead, the charge is spread over many solvent molecules (5-10) and strongly interacts with their valence electrons. More often than not, these multimer anions and cations have unusual dynamical properties: for example, their diffusion rate is many times greater than the rate of molecular diffusion in a given solvent. This diffusion is due to ultrafast degenerate charge hopping. Our recent examples of such high-mobility species are multimer cations in cycloalkanes and multimer anions in supercritical CO_2 and the "organic water", acetonitrile. The latter provides the only known example of a liquid that yields *two* metastable reducing species: the high-mobility multimer anion and the normally diffusing dimer radical anion. Our studies suggest that the formation of such multimer anions/cations, rather than "solvated electrons" and/or molecular radical ions, is the preferred mode for stabilization of the excess negative/positive charge in the majority of molecular liquids, including most important industrial solvents.